

SODIUM GALLIUM OXIDE ELECTROLYTE  
ADDITIVE FOR ALUMINUM ANODE ACTIVATION

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) LOUIS G. CARREIRO, and (2) STEVEN P. TUCKER, citizens of the United States of America, employees of the United States Government, residents (1) Westport, County of Bristol, Commonwealth of Massachusetts and (2) Portsmouth, County of Newport, State of Rhode Island, have invented certain new and useful improvements entitled as set forth above of which the following is a specification:

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ADDITIVE FOR ALUMINUM ANODE ACTIVATION

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

CROSS REFERENCE TO OTHER PATENT APPLICATIONS

Not applicable.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention generally relates to an electrolyte additive for aluminum anode activation.

More particularly, the invention relates to an electrolyte additive for aluminum anode activation in which the additive is sodium gallium oxide, the additive preventing or reducing the formation of an oxide coating on a surface of a metal.

(2) Description of the Prior Art

In the current art of aluminum based semi-fuel cells (Al-SFC), elemental aluminum (or one of its alloys) along with hydrogen peroxide, is consumed to produce energy. Among the

1 more promising semi-fuel cells currently being considered as  
2 electrochemical sources is the aluminum/hydrogen peroxide  
3 cell. The type of aluminum used in the semi-fuel cell is  
4 dictated by the specific requirements of the application.  
5 Applications requiring high discharge rates (current densities  
6 above 1000 mA/cm<sup>2</sup>), typically utilize aluminum-based alloys  
7 such as XA5-P and DF50V, while for low rate (current densities  
8 from 5-50 mA/cm<sup>2</sup>) applications, EB50V is the aluminum alloy of  
9 choice.

10 All three proprietary alloys are formulated by ALCAN  
11 International; however, consideration of these alloys for  
12 further use is jeopardized by the following facts: (a) EB50V,  
13 XA5-P, and DF50V are proprietary alloys manufactured by a sole  
14 source, and (b) the present state of the economy (supply and  
15 demand) has forced the cost of these unique alloys to  
16 prohibitive and costly levels beyond acceptable acquisition  
17 levels. For these reasons, pure aluminum has been  
18 investigated as a replacement for the costly and difficult to  
19 acquire proprietary alloys.

20 The use of pure aluminum metal (especially in low rate  
21 semi-fuel cell systems) is hindered by the fact that aluminum  
22 readily oxidizes in a caustic electrolyte, thereby forming a  
23 passive surface layer that causes its chemical reactivity to  
24 greatly diminish, and adversely affecting the power output and  
25 efficiency of the semi-fuel cell. It was found by the  
26 inventors that an addition of gallium ions to the electrolyte

1 solution prevents aluminum oxide formations, and hence  
2 eliminates the problem of passivity.

3 The use of electrolyte additives to modify the chemical  
4 reactivity of aluminum metal and aluminum-based alloys used as  
5 anodes in semi-fuel cells has been previously investigated for  
6 high rate applications in each of the following publications:

7 *Enhanced Electrochemical Performance in the*  
8 *Development of the Aluminum/Hydrogen Peroxide Semi-Fuel Cell*  
9 by E.G. Dow et. al., Journal of Power Sources 65 (1997) pp.  
10 207-212.

11 *Aluminum-Hydrogen Peroxide Battery Development: Part*  
12 *II - Anode Polarization of Pure Aluminum Via Electrolyte*  
13 *Additives*, Seebach et. al., Technical Memorandum of NAVAL  
14 UNDERWAEA WARFARE CENTER DIVISION NEWPORT, RHODE ISLAND, 15  
15 June 1992.

16 *Electrochemical Characterization of aluminym alloy*  
17 *EB50V: The Effect of Sodium Hydroxide Concentration,*  
18 *Aluminate Concentration, Stannate Concentration, and*  
19 *Temperature*, Medeiros et al., 18 January 1993, Technical  
20 Memorandum of NAVAL UNDERWAEA WARFARE CENTER DIVISION NEWPORT,  
21 RHODE ISLAND.

22 For the most part, these studies utilized half-cell  
23 reaction experiments to obtain polarization data (i.e.,  
24 current-voltage curves) that was correlated to changes in  
25 aluminum activity as a function of electrolyte additive.  
26 Several electrolyte additives in the form of metal oxides were  
27 tested and it was found that gallium oxide yielded the best

1 anodic voltage, -1.3 volts versus Af/AgCl at 400 mA/cm<sup>2</sup>.  
2 However, since gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) has limited solubility in  
3 caustic (seawater/sodium hydroxide) electrolytes typically  
4 used in aluminum based semi-fuel cells, it is difficult to  
5 quantify and/or control the effect that the gallium ion has on  
6 the electrochemical performance of aluminum, i.e. to determine  
7 the optimum gallium concentration required to prevent aluminum  
8 passivity. Accordingly, a need still exists in the art for a  
9 suitable additive having the desired properties.

10 The following patents, for example, discuss the  
11 prevention of corrosion by producing a protective oxide  
12 coating on the surface of a metal such as aluminum. However,  
13 these patents do not teach the prevention of formation of such  
14 a surface in the first place as does the present invention.

15  
16 U.S. Patent No. 3,347,155 to Weber;

17 U.S. Patent No. 3,887,399 to Gunn; and

18 U.S. Patent No. 6,030,517 to Lincot et al.

19 Specifically, Weber discloses a process of improving the  
20 corrosion resistance of aluminum articles that includes  
21 removing the impurities from the article surface, then  
22 chemically or electrolytically forming an artificial aluminum  
23 oxide coating, treating the artificially oxide coated article  
24 to a dilute aqueous solution of an inorganic base such as NaOH  
25 or KOH, and thereafter treating the article to an alkaline  
26 silicate solution. Advantageously intermediate the above  
27 mentioned treatments, the article is treated to one or more of

1 aqueous solutions of (1) organic compounds having cations of  
2 various iron group metals and anions of acetates, citrates,  
3 oxalates, tartrates, (2) organic compounds of various alkali  
4 and alkali earth metals having anions of acetates, citrates,  
5 oxalates, (3) ammonium hydroxide, (4) ammonium compounds  
6 having an anion of such acetates, citrates, carbonates, and  
7 (5) various mixtures of the above.

8       The patent to Gunn discloses a multi-chambered  
9 incinerator having high temperature electric heater elements  
10 at one or more flame ports. The incinerator has a main  
11 combustion chamber followed by one or more additional chambers  
12 connected by one or more flame ports. In the flame port that  
13 may have checkerboarded refractory or a high temperature, an  
14 electric heater grid system of elongated heater elements is  
15 installed. The electric heater elements are designed for  
16 rapid rise in temperature, for example in a period of 5 to 15  
17 minutes to provide flame port temperatures in the order of  
18 1300°F more or less depending on operating conditions. The  
19 elongated electric heater elements, which can be arranged  
20 either vertically or horizontally or as a grid system, provide  
21 an extremely rapid rise high temperature heating element to  
22 facilitate the combustion of waste materials and gases and  
23 particulates and further serves as an impingement screen to  
24 provide for settling of incombustible particulates. The  
25 electric heater system can be used with or without  
26 checkerboard refractory in the flame ports and provides an  
27 improved and efficient means for incinerating industrial,

1 commercial or agricultural waste material and minimizes air  
2 pollution.

3 The patent to Lincot et al. discloses a process for  
4 depositing a film of a metal oxide or that of a metal  
5 hydroxide on a substrate in an electrochemical cell, wherein  
6 (i) the metal hydroxide is of formula  $M(OH)_x A_y$ , M representing  
7 at least one metallic species in an oxidation state i chosen  
8 from the elements in Groups II and III of the periodic Table,  
9 A being an anion whose number of charges n,  $0 < x \leq 1$  and  $x + ny = 1$ ,  
10 (ii) the electrochemical cell comprises (a) an electrode  
11 comprising the substrate, (b) a counter-electrode, (c) a  
12 reference electrode and (d) an electrolyte comprising a  
13 conducting solution comprising at least one salt of the metal  
14 M, the process comprising the steps of: dissolving oxygen in  
15 the electrolyte and imposing a cathode potential of less than  
16 the oxygen reduction potential and greater than the potential  
17 for deposition of the metal M in the electrolyte in question  
18 on the electrochemical cell.

19 It should be understood that the present invention would  
20 in fact enhance the functionality of the above patents as  
21 follows: In contrast to the aforementioned patents, the  
22 intent of the present invention is not to produce a protective  
23 oxide coating on the surface of a metal such as aluminum but  
24 instead to prevent or reduce one such oxide coating from  
25 forming. In a semi-fuel cell (SCF), aluminum reacts with an  
26 alkaline solution such as sodium hydroxide to form an unwanted  
27 aluminum oxide layer. Since this oxide layer inhibits the

1 electrochemical reactivity of the aluminum resulting in lower  
2 semi-fuel cell efficiency, it must be eliminated or minimized.  
3 The invention described herein utilizes a specific ternary  
4 compound, sodium gallate ( $\text{NaGaO}_2$ ) that will dissolve in  
5 alkaline electrolytes and in the presence of aluminum metal  
6 will prevent an oxide coating from forming on the surface of  
7 the aluminum.

#### 8 9 SUMMARY OF THE INVENTION

10 Therefore it is an object of this invention to provide an  
11 electrolyte additive for aluminum anode activation.

12 Another object of this invention is to provide an  
13 electrolyte additive for aluminum anode activation in which  
14 the additive prevents or reduces formation of an oxide coating  
15 on a surface of a metal.

16 Still another object of this invention is to provide an  
17 electrolyte additive for aluminum anode activation in which  
18 the additive is sodium gallium oxide.

19 In accordance with one aspect of this invention, there is  
20 provided an additive for an aluminum-based semi-fuel cell  
21 system includes a combination of components including gallium,  
22 oxygen, and a sodium component dissolvable in an alkaline  
23 electrolyte solution such as seawater and sodium hydroxide.  
24 These components form sodium gallium oxide and prevent  
25 formation of an oxide layer on a surface of an aluminum anode  
26 in the alkaline electrolyte of the semi-fuel cell system.



DESCRIPTION OF THE PREFERRED EMBODIMENT

In general, the present invention is directed to a new electrolyte additive, sodium gallium oxide ( $\text{NaGaO}_2$ ), intended for use as an activator in aluminum-based semi-fuel cell (Al-SFC) systems.

Sodium gallium oxide, when dissolved in the caustic solution of the aluminum based semi-fuel cell, produces  $\text{FA}(\text{III})$  ions that prevent or inhibit the formation of an oxide layer on the surface of the aluminum anode. Since the formation of surface oxide is detrimental to the performance and efficiency of the aluminum based semi-fuel cell it must be eliminated or minimized.

This invention describes the use of a sodium gallium oxide ( $\text{NaGaO}_2$ ) as an electrolyte additive in aluminum based semi-fuel cell systems. Although sodium gallium oxide is not available as an off-the shelf reagent, it can be easily prepared by the solid state reaction:

sodium oxalate + gallium oxide  $\xrightarrow{1200^\circ\text{C}}$  sodium gallium oxide + carbon dioxide

Sodium gallium oxide ( $\text{NaGaO}_2$ ) is dissolved in the seawater/sodium hydroxide electrolyte in the anode compartment of the aluminum based semi-fuel cell. The concentration of the  $\text{NaGaO}_2$  ranges from  $1.0 \times 10^{-5} \text{ M}$  to  $3.0 \times 10^{-5} \text{ M}$ ; whereas  $\text{M}$  is molarity and  $5\text{M}$  indicates the concentration of  $\text{NaGaO}_2$  to be five times its molecular weight in grams (one mole) per liter of solution. The anode consists of pure aluminum (purity, 99.99% to 99.999%) and sodium tin oxide ( $0.01 \text{ M}$  to  $0.03 \text{ M}$ ).

1 [It should be noted that concentration of solution as that  
2  $\text{NaGaO}_2$  is defined in terms of M, molarity which is indicated by  
3 molarity, M].

4 The use of  $\text{NaGaO}_2$  as an electrolyte additive allows less  
5 expensive, readily available aluminum metal to be used as the  
6 anode material in aluminum based semi-fuel cells. The major  
7 advantage of sodium gallium oxide is its solubility in caustic  
8 electrolytes. Unlike gallium oxide ( $\text{Ga}_2\text{O}_3$ ), which has a  
9 limited solubility, sodium gallium oxide dissolves completely  
10 allowing its exact concentration in solution to be determined.  
11 Other advantages are that the sodium gallium oxide is in its  
12 solid powder form at room temperature, is stable in air, and  
13 has no special storage requirements.

14 Additional compounds which could also find applications  
15 as electrolyte additives for aluminum based semi-fuel cells  
16 include  $\text{NaGa}_3\text{O}_8$ ,  $\text{KGa}_5\text{O}_8$ ,  $\text{KGa}_{11}\text{O}_{17}$ ,  $\text{Ga}(\text{NO}_3)_3$ .

17 In view of the above detailed description, it is  
18 anticipated that the invention herein will have far reaching  
19 applications other than those of aluminum based semi-fuel  
20 cells.

21 This invention has been disclosed in terms of certain  
22 embodiments. It will be apparent that many modifications can  
23 be made to the disclosed apparatus without departing from the  
24 invention. As an example, any of the above-mentioned  
25 additives can be prepared by different methods for use to  
26 prevent or reduce the formation of an oxide layer on the  
27 aluminum anode surface. Therefore, it is the intent of the

- 1 appended claims to cover all such variations and modifications
- 2 as come within the true spirit and scope of this invention.